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A method of dry cleaning fabrics using densified carbon dioxide

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A METHOD OF DRY CLEANING FABRICS USING DENSIFIED CARBON DIOXIDE

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TECHNICAL FIELD

5 The present invention provides a method for the removal of stains from fabric ⁽⁸⁶⁾ densified carbon dioxide. More particularly the invention is concerned with a method of dry cleaning fabric comprising the successive steps of contacting the fabric with a fluid dry cleaning composition containing densified carbon dioxide at a temperature between -20 and 60°C and a pressure between 1 and 100 MPa., so as to allow stains to dissolve and/or to
10 disperse into the fluid dry cleaning composition, and separating the fabric and the fluid dry cleaning composition, wherein the fluid dry cleaning composition contains a surfactant.

BACKGROUND OF THE INVENTION

 Densified, particularly supercritical fluid, carbon dioxide has been suggested as an
15 alternative to halocarbon solvents used in conventional dry cleaning.

 Densified carbon dioxide provides a nontoxic, inexpensive, recyclable and environmentally acceptable solvent to remove soils in the dry cleaning process. The supercritical carbon dioxide has been shown to be effective in removing nonpolar stains such as motor oil, when combined with a viscous cleaning solvent, particularly mineral oil or
20 petrolatum as described in U.S. 5,279,615

 The solvent power of densified carbon dioxide is low relative to ordinary liquid solvents and the carbon dioxide solvent alone is less effective on hydrophilic stains such as grape juice, coffee and tea and on compound hydrophobic stains such as lipstick and candle wax, unless surfactants and solvent modifiers are added.

25 A cleaning system combining particular anionic or nonionic surface active agents with supercritical fluid carbon dioxide is described in DE-A 39 04 514. These anionic and nonionic agents, such as alkylenebenzene sulfates and sulfonates, ethoxylated alkylene phenols and ethoxylated fatty alcohols, were particularly effective when combined with a relatively large amount of water (greater than or equal to 4%).

30 US 5,683,472 relates to a method of dry cleaning fabrics using a dry cleaning system that comprises densified carbon dioxide and a surfactant which is soluble in the densified carbon dioxide and which has a polysiloxane, a branched polyalkylene oxide or a halocarbon group which is a functional CO₂-philic moiety connected to a CO₂-phobic functional moiety.

US 6,200,352 describes a method of dry cleaning articles such as fabrics and clothing with the help of a liquid dry cleaning composition that comprises a mixture of carbon dioxide, a surfactant and an organic co-solvent. The preferred surfactant is one that does not contain a CO₂-philic group.

5 The dry cleaning systems using densified carbon dioxide known in the art suffer from the drawback that, although they may effectively be used to remove certain types of stains, they are incapable of effectively removing all sorts of stains including nonpolar stains (e.g. those made by a nonpolar organic component such as mineral oil, vegetable oil, sebum etc.), polar stains (e.g. grape juice, coffee and tea stains), compound hydrophobic stains (e.g. stains
10 from lipstick and candle wax) as well as particulate soils (e.g. soils containing insoluble solid components such as silicates, carbon black etc.).

The present invention provides an improved dry cleaning method that utilises densified carbon dioxide and a special surfactant which method offers the advantage that it can be used to effectively remove all sorts of stains from fabrics.

15

SUMMARY OF THE INVENTION

The inventors have surprisingly discovered that in a method of dry cleaning fabrics with a densified carbon dioxide composition, the use of an ionic surfactant, e.g. a surfactant that contains a lipophilic alkyl residue and a polar amine or carboxylate residue, produces
20 exceptionally good cleaning results if said surfactant is employed in an amount that exceeds its maximum solubility in the densified carbon dioxide composition. It was unexpectedly found that the resulting presence of undissolved ionic surfactant makes it possible to effectively remove all sorts of stains, ie. polar, nonpolar, compound stains and in particular soils.

25 Although the inventors do not wish to be bound by theory it is believed that the exceptionally good results obtained with the present method are partly due to the ability of the ionic surfactant to charge the fabric as well as the stains, and to thus facilitate the removal of the stains as a result of the ensuing electrostatic repulsive forces. The presence of a significant amount of undissolved ionic surfactant somehow reinforces this detergent effect of the
30 surfactant, but the mechanism by which this is achieved is as yet unknown.

DETAILED DESCRIPTION OF THE INVENTION

Accordingly the present invention relates a method of dry cleaning fabric comprising the successive steps of:

a) contacting the fabric with a fluid dry cleaning composition containing densified carbon dioxide at a temperature between -20 and 60°C and a pressure between 1 and 100 MPa., so as to allow stains to dissolve and/or to disperse into the fluid dry cleaning composition and

5 b) separating the fabric and the fluid dry cleaning composition; wherein the fluid dry cleaning composition comprises an ionic surfactant in a concentration of between 0.01 and 15% by weight of the carbon dioxide and wherein during step a) at least 10%, preferably at least 30% of said ionic surfactant is present in undissolved form.

10 The term "ionic surfactant" as used herein refers to surfactants that are either positively charged (cationic surfactants) or negatively charged (anionic surfactants) at the conditions applied in step a). Best results are obtained with the present method if the ionic surfactant is classified as a cationic surfactant when applied in water.

15 The term "cleaning" as used herein refers to any removal of soil, dirt, grime, or other unwanted material, whether partial or complete. The present method may be used to clean nonpolar stains, polar stains, compound hydrophobic stains and particulate soils. Examples of articles that can suitably be cleaned by the method of the invention include woven and non-woven fabrics formed from materials such as cotton, wool, silk, leather, rayon, polyester, acetate, fiberglass, furs, etc. These fabrics may have been formed into items such as clothing, work gloves, rags, leather goods (e.g. handbags and brief cases), etc.

20 In order to provide sufficient time to allow stains to dissolve and/or to disperse into the fluid dry cleaning it is preferred that the duration of step a) exceeds 2 minutes; preferably 5 minutes.

25 The results obtained with the present method are very dependent on the type of ionic surfactant used. Very good results are obtained with a ionic surfactant that contains a lipophilic, optionally heterogeneous hydrocarbyl residue with 3-25 carbon atoms and a polar amine, phosphate, phosphonate, phosphinate, sulphate, sulphonate, sulphinate, or carboxylate group. The aforementioned polar groups may be employed in protonated or salt form, e.g. as salts with monovalent cations such as sodium, potassium and ammonium, or as salts with divalent cations such as magnesium and calcium. Exceptionally good results can be achieved with an ionic surfactant that is represented by the formula R_1-X , R_1-Y-R_2 or $R_1-Z(R_2)-R_3$,
30 wherein:

R_1 , R_2 and R_3 independently are a substituted or unsubstituted, linear or branched, optionally heterogeneous C_3-C_{22} alkyl; a substituted or unsubstituted, optionally heterogeneous C_3-C_{16}

cycloalkyl; a substituted or unsubstituted, linear or branched, optionally heterogeneous C₃-C₂₂ alkenyl; or a substituted or unsubstituted, optionally heterogeneous aryl; and wherein X is NH₂, PO₄M₂, PO₃M₂, PO₂M₂, SO₄M, SO₃M, SO₂M or COOM;

Y is NH, PO₄M, PO₃M, PO₂M, SO₄, SO₃, SO₂, or COO;

5 Z is N, PO₄, PO₃, or PO₂;

and M represents sodium, potassium, ammonium or hydrogen.

Best results are obtained with the present invention if the ionic surfactant is represented by the formula R₁-X or R₁-Y-R₂, wherein X is NH₂ or COOM and Y is NH. Most preferably X is NH₂ and Y is NH. In another preferred embodiment R₁, R₂ and R₃

10 independently are a substituted or unsubstituted, linear or branched, optionally heterogeneous C₈-C₂₂ alkyl or are a substituted or unsubstituted, linear or branched, optionally heterogeneous C₈-C₂₂ alkenyl. The liquid dry-cleaning compositions useful for carrying out the present invention typically include some water. The source of the water is not critical in all applications. The water may be added to the liquid solution before the articles to be cleaned
15 are deposited therein, or may be atmospheric water, or may be the water carried by the garments, etc.

In one embodiment of the invention, better particulate cleaning may be obtained in the absence of water added to the dry-cleaning composition. There is inherently water present on or in the garments or articles to be cleaned as they are placed in the cleaning vessel. This
20 water serves in part to adhere particulate soil to the articles to be cleaned. As the water is removed from the garments into the cleaning composition during the cleaning process, the removal of water from the article to be cleaned facilitates the removal of particulates from the articles to be cleaned. Thus, decreasing the amount of water originally in the cleaning system can serve to facilitate the cleaning of particulate soil from the articles to be cleaned by the
25 action of the water inherently carried by the article to be cleaned.

According to a preferred embodiment of the present method, the fluid dry cleaning composition contains less than 10 wt.% water. More preferably the composition contains less than 6 wt.% water. Most preferably the water content of the dry cleaning composition is between 0.0001 and 5 wt.%. Here the dry water content relates to the total dry water content
30 of the composition, i.e. water that may originate from different sources (e.g. the fabric) as described above.

In a preferred embodiment of the present method in addition to carbon dioxide one or more other components that have densified properties are employed in the fluid dry cleaning mixture. Suitable examples of such a densified component include methane, ethane, propane,

, butane, n-pentane, n-hexane, cyclohexane, n-heptane, ethylene, propylene, methanol, ethanol, isopropanol, n-propanol, benzene, toluene, p-xylene, sulfur dioxide,

chlorotrifluoromethane, trichlorofluoromethane, perfluoropropane, chlorodifluoromethane, sulfur hexafluoride and nitrous oxide. Preferably the fluid dry cleaning composition contains
5 between 0.1 to 10 wt.% of a such a densified component. The preferred densified component is a C₁-C₆ alcohol or diol. More preferably the co-solvent is a C₁-C₅ alcohol. Most preferably the co-solvent is a C₂-C₄ alcohol.

The fluid dry cleaning composition used in the present method may also contain an organic co-solvent, particularly a hydrocarbon co-solvent. Examples of suitable co-solvents
10 include, but are not limited to, aliphatic and aromatic hydrocarbons, and esters and ethers thereof, particularly mono and di-esters and ethers (e.g., EXXON ISOPAR L, ISOPAR M, ISOPAR V, EXXON EXXSOL, EXXON DF 2000, CONDEA VISTA LPA-170N, CONDEA VISTA LPA-210, cyclohexanone, and dimethyl succinate), alkyl and dialkyl carbonates (e.g., dimethyl carbonate, dibutyl carbonate, di-t-butyl dicarbonate, ethylene carbonate, and
15 propylene carbonate), alkylene and polyalkylene glycols, and ethers and esters thereof (e.g., ethylene glycol-n-butyl ether, diethylene glycol-n-butyl ethers, propylene glycol methyl ether, dipropylene glycol methyl ether, tripropylene glycol methyl ether, and dipropylene glycol methyl ether acetate), lactones (e.g., (gamma)butyrolactone, (epsilon)caprolactone, and (delta) dodecanolactone), alcohols and diols (2-methoxy-2-propanol, 1-octanol, 2-ethyl hexanol, cyclopentanol, 1,3 -propanediol, 2,3-butanediol, 2-methyl-2,4-pentanediol) and
20 polydimethylsiloxanes (e.g., decamethyltetrasiloxane, decamethylpentasiloxane, and hexamethyldisiloxane), etc.

As will be apparent to those skilled in the art, numerous additional ingredients can be included in the present fluid dry cleaning composition, including detergents, bleaches,
25 whiteners, softeners, sizing, starches, enzymes, hydrogen peroxide or a source of hydrogen peroxide, fragrances, etc.

The present method is suitably carried out at around room temperature. Hence, in a preferred embodiment the method comprises contacting the fabric with the fluid dry cleaning composition at a temperature between 0 and 30°C. Similarly, in a preferred embodiment step
30 a) comprises contacting the fabric with the fluid dry cleaning composition at a pressure between 2 and 25 MPa.

In practice, in a preferred embodiment of the invention, the fabric to be cleaned and the fluid dry cleaning composition are combined in a closed drum. The liquid dry cleaning composition is preferably provided in an amount so that the closed drum contains both a

liquid phase and a vapour phase (that is, so that the drum is not completely filled with the article and the liquid composition). The fabric article is then agitated in the drum, preferably so that the article contacts both the liquid dry cleaning composition and the vapor phase, with the agitation carried out for a time sufficient to clean the fabric. The cleaned article is then removed from the drum. The article may optionally be rinsed (for example, by removing the composition from the drum, adding a rinse solution such as liquid carbon dioxide (with or without additional ingredients such as water, co-solvent, etc.) to the drum, agitating the article in the rinse solution, removing the rinse solution, and repeating as desired), after the agitating step and before it is removed from the drum. The dry cleaning, compositions and the rinse solutions may be removed by any suitable means, including both draining, and venting. Any suitable cleaning, apparatus may be employed, including both horizontal drum and vertical drum apparatus. When the drum is a horizontal drum, the agitating step is carried out by simply rotating the drum. When the drum is a vertical drum it typically has an agitator positioned therein, and the agitating step is carried out by moving, (e.g., rotating, or oscillating) the agitator within the drum. A vapour phase may be provided by imparting sufficient shear forces within the drum to produce cavitation in the liquid dry-cleaning composition. Finally, in an alternate embodiment of the invention, agitation may be imparted by means of jet agitation as described in U.S. Pat. No. 5,467,492 to Chao et al., the disclosure of which is incorporated herein by reference. As noted above, the liquid dry cleaning, composition is preferably an ambient temperature composition, and the agitating step is preferably carried out at ambient temperature, without the need for associating a heating, element with the cleaning apparatus.

The invention is further illustrated by means of the following examples.

EXAMPLES

Example 1

The experiment is carried out in a vessel of 25 litres with a rotating drum of 10 litres. The vessel has two viewing glasses to monitor the behaviour of the fluid. During the cleaning and rinsing cycle the rotating drum is alternately rotated clockwise for 30 seconds and counter clockwise for 30 seconds both at a speed of 75 cycles per minute. The dry-cleaning fluid is circulated over the vessel using a centrifugal pump. The piping from the vessel towards the pump contains a filter, while the piping from the pump towards the vessel contains a heat

exchanger to control the temperature of the whole system. The equipment contains a mass flow meter, a temperature indicator and a pressure indicator.

During the cleaning cycle the rotating drum is filled with ten small pre-stained test fabrics. These stained test fabrics are:

5

	STAIN	FABRIC
1	sebum and carbon black	wool
2	sebum and carbon black	polyester
3	egg yolk	wool
4	egg yolk	polyester
5	butterfat with colorant	cotton
6	butterfat with colorant	polyester/cotton blend
7	vegetable oil with chlorophyll	cotton
8	vegetable oil with chlorophyll	polyester/cotton blend
9	clay	wool
10	clay	polyester

The test fabrics were attached to an additional load of 400 grams of white cotton fabrics. The stained test fabrics were analysed before and after the cleaning cycle to determine the coloration change of the fabrics. The values were expressed in Lab values. The absolute colour difference between two samples in the Lab space is expressed as:

$$\Delta E = \sqrt{\Delta L^2 + \Delta a^2 + \Delta b^2}.$$

To examine the efficiency of the cleaning, both the cleaned and stained fabrics are compared with the original unstained fabric, leading to the absolute colour difference $\Delta E_{\text{stained}}$ and $\Delta E_{\text{cleaned}}$. The cleaning performance index of an experiment is expressed as:

$$CPI_{\text{Lab}} = \left(1 - \frac{\Delta E_{\text{cleaned}}}{\Delta E_{\text{stained}}} \right) \times 100\%.$$

When the fabric is clean the CPI_{lab} value is 100%, when the cleaning has no effect the value is 0%.

The cleaning is started by filling the vessel at ambient conditions with the additional load and the attached stained test fabrics. Subsequently a cleaning liquid comprising of 250 grams of iso-propanol, 25 grams water and 39 gram of dissolved dodecylamine, was added to

the fabric load. The vessel was closed and pressurised with 6 kg of liquid carbon dioxide from a storage tank. The system reached a pressure of 48 bars and a temperature of 12 °C. Through the viewing glasses it was observed that a large fraction of the dodecylamine precipitates as small particles. This is caused by the fact that dodecylamine has a limited solubility in carbon dioxide. The rotating drum was started and the fabric is cleaned for 30 minutes. After the cleaning the vessel was rinsed with 12 kg of fresh carbon dioxide from the storage vessel for 10 minutes, while keeping the system at 48 bars. Subsequently the vessel was depressurised after which it was opened, the cleaned fabrics were taken out and the colour differences were measured. The CPI_{lab} values obtained are shown in the table below.

Example 2

Example 1 was repeated except that the cleaning liquid was composed of 250 grams iso-propanol, 25 grams water and 40 grams of dissolved dioctylamine. The vessel was closed and pressured with 6 kg of liquid carbon dioxide from a storage tank. The system reached a pressure of 48 bars and a temperature of 12 °C. Through the viewing glass it was observed that a large amount of the dioctylamine precipitated as small particles. After the cleaning, the vessel was rinsed and depressurised as described in example 1. The CPI_{lab} values found for each of the test fabrics are shown in the table below.

Example 3

Example 1 was repeated except that this time 50 grams of solid sodium stearate and 25 grams of water were put in the cleaning vessel. The vessel was closed and pressurised with 4 kg of liquid carbon dioxide from a storage tank. The system reached a pressure of 46 bars and a temperature of 10 °C. Through the viewing glass it was observed that a large amount of sodium stearate did not dissolve in the carbon dioxide. After the cleaning, the vessel was rinsed and depressurised as described in example 1. The CPI_{lab} values found for each of the test fabrics are shown in the table below.

Example 4

Example 1 was repeated except that this time 10 grams of solid sodium dodecyl sulfate and 25 grams of water were put in the cleaning vessel. The vessel was closed and pressurised with 6 kg of liquid carbon dioxide from a storage tank. The system reached a pressure of 46 bars and a temperature of 11 °C. Through the viewing glass it was observed that a large amount of sodium dodecyl sulfate did not dissolve in the carbon dioxide. After the cleaning,

the vessel was rinsed and depressurised as described in example 1. The CPI_{lab} values found for each of the test fabrics are shown in the table below.

5 Example 5

Example 1 was repeated except that the cleaning liquid was composed of 250 grams of iso-propanol, 25 grams water and 10 grams of tribenzylamine. The vessel was closed and pressurised with 6 kg of liquid carbon dioxide from a storage tank. The system reached a pressure of 45 bars and a temperature of 10 °C. Through the viewing glass it was observed
10 that a large amount of tribenzylamine precipitated as small particles. After the cleaning, the vessel was rinsed and depressurised as described in example 1. The CPI_{lab} values found for each of the test fabrics are shown in the table below.

Example 6

15 Example 1 was repeated except that the cleaning liquid was composed of 255 grams of iso-propanol, 25 grams water and 1 grams of octadecylamine. The vessel was closed and pressurised with 6 kg of liquid carbon dioxide from a storage tank. The system reached a pressure of 48 bars and a temperature of 12 °C. Through the viewing glass it was observed that a very small amount of the octadecylamine precipitated as small particles. After the
20 cleaning, the vessel was rinsed and depressurised as described in example 1. The CPI_{lab} values found for each of the test fabrics are shown in the table below.

Example 7

25 Example 6 was repeated except that the cleaning liquid was composed of 251 grams of iso-propanol, 25 grams water and 5 grams of octadecylamine. The vessel was closed and pressurised with 6 kg of liquid carbon dioxide from a storage tank. The system reached a pressure of 46 bars and a temperature of 11 °C. Through the viewing glass it was observed that a small amount of the octadecylamine precipitated as small particles. After the cleaning, the vessel was rinsed and depressurised as described in example 1. The CPI_{lab} values found
30 for each of the test fabrics are shown in the table below.

Example 8

Example 6 was repeated except that the cleaning liquid was composed of 250 grams of iso-propanol, 25 grams water and 10 grams of octadecylamine. The vessel was closed and

pressurised with 6 kg of liquid carbon dioxide from a storage tank. The system reached a pressure of 48 bars and a temperature of 12 °C. Through the viewing glass it was observed that a substantial amount of octadecylamine precipitated as small particles. After the cleaning, the vessel was rinsed and depressurised as described in example 1. The CPI_{lab} values found for each of the test fabrics are shown in the table below.

Example 9

Example 6 was repeated except that the cleaning liquid was composed of 250 grams of iso-propanol, 30 grams water and 40 grams of octadecylamine. The vessel was closed and pressurised with 6 kg of liquid carbon dioxide from a storage tank. The system reached a pressure of 46 bars and a temperature of 11 °C. Through the viewing glass it was observed that a large amount of octadecylamine precipitated as small particles. After the cleaning, the vessel was rinsed and depressurised as described in example 1. The CPI_{lab} values found for each of the test fabrics are shown in the table below.

Comparative example A

Example 1 was repeated except that no cleaning liquid was put in the vessel. The vessel was closed and pressured with 12 kg of liquid carbon dioxide from a storage tank. The system reached a pressure of 45 bars and a temperature of 10 °C. After the cleaning, the vessel was rinsed and depressurised as described in example 1. The CPI_{lab} values found for each of the test fabrics are shown in the table below.

The cleaning performance (expressed as CPI_{lab} values) achieved in each of the cleaning cycles described in the aforementioned examples is summarised in the following table:

	EXAMPLES									
	1	2	3	4	4	6	7	8	9	A
Sebum on Wool	74	76	63	44	58	55	57	79	89	30
Sebum on Polyester	46	44	44	23	40	36	42	48	58	21
Egg-yolk on wool	64	62	46	56	47	60	60	62	64	41
Egg-yolk on polyester	50	55	40	49	38	51	48	49	53	37
Butterfat on cotton	80	90	72	88	62	84	86	86	84	65
Butterfat on blend fabric	87	93	83	92	76	89	89	90	87	80
vegetable oil on cotton	57	67	41	64	27	55	51	61	65	16
vegetable oil on blend fabric	20	20	27	26	19	22	15	24	23	6
Clay on wool	68	62	52	32	66	43	35	44	47	11
Clay on polyester	12	11	27	2	39	13	9	2	12	7

The above results show that the addition of an ionic surfactant dramatically improves the cleaning performance. The examples 1, 2, 3, 4, 5 and 9 illustrate that the benefits of the present invention may be obtained with different types of ionic surfactants, even though the improved cleaning performance may manifest itself in different ways. The results also shown that the amines are particularly effective. The examples 6, 7, 8 and 9 show that an increase of the concentration of the surfactant increases the cleaning performance of the washing cycle. This is a surprising finding since the applied amount of dissolved surfactant is the same in all these samples. All examples show that especially the removal of particulate soils is improved dramatically.

CLAIMS

1. A method of dry cleaning fabric comprising the successive steps of:
 - 5 a) contacting the fabric with a fluid dry cleaning composition containing densified carbon dioxide at a temperature between -20 and 60°C and a pressure between 1 and 100 MPa., so as to allow stains to dissolve and/or to disperse into the fluid dry cleaning composition and
 - b) separating the fabric and the fluid dry cleaning composition;
- 10 wherein the fluid dry cleaning composition comprises an ionic surfactant in a concentration of between 0.01 and 15% by weight of the carbon dioxide and wherein during step a) at least 10%, preferably at least 30% of said ionic surfactant is present in undissolved form.
2. The method according to claim 1, wherein the ionic surfactant is classified as a
 - 15 cationic surfactant when applied in water.
3. The method according to claim 1 or 2, wherein the duration of step a) exceeds 2 minutes, preferably 5 minutes.
- 20 4. The method according to any one of claims 1-3, wherein the ionic surfactant contains one or more lipophilic hydrocarbyl residues with 3-25 carbon atoms and a polar amine, phosphate, phosphonate, phosphinate, sulphate, sulphonate, sulphinate or carboxylate group.
5. The method according to any one of claims 1-4, wherein the ionic surfactant is
 - 25 represented by the formula R_1-X , R_1-Y-R_2 or $R_1-Z(R_2)-R_3$, wherein:
 R_1 , R_2 and R_3 independently are a substituted or unsubstituted, linear or branched, optionally heterogeneous C_3-C_{22} alkyl; a substituted or unsubstituted, optionally heterogeneous C_3-C_8 cycloalkyl; a substituted or unsubstituted, linear or branched, optionally heterogeneous C_3-C_{22} alkenyl; or a substituted or unsubstituted, optionally heterogeneous aryl; and wherein
 - 30 X is NH_2 , PO_4M_2 , PO_3M_2 , PO_2M_2 , SO_4M , SO_3M , SO_2M or $COOM$;
 Y is NH , PO_4M , PO_3M , PO_2M , SO_4 , SO_3 , SO_2 , or COO ;
 Z is N , PO_4 , PO_3 , or PO_2 ;
 and M represents sodium, potassium, ammonium or hydrogen.

6. The method according to claim 5, wherein the ionic surfactant is represented by the formula R_1-X or R_1-Y-R_2 , wherein X is NH_2 or $COOM$ and Y is NH .
7. The method according to claim 5, wherein R_1 , R_2 and R_3 independently are a substituted or unsubstituted, linear or branched, optionally heterogeneous C_8-C_{22} alkyl or are a substituted or unsubstituted, linear or branched, optionally heterogeneous C_8-C_{22} alkenyl.
8. The method according to any one of claims 1-7, wherein the fluid dry cleaning composition contains between 0.03 and 5 wt.% water.
9. The method according to any one of claims 1-8, wherein the fluid dry cleaning composition contains between 0.3 to 10 wt.% of a C_1-C_{15} alcohol.
10. The method according to any one of claims 1-9, wherein step a) comprises contacting the fabric with the fluid dry cleaning composition at a temperature between 0 and 30°C.
11. The method according to any one of claims 1-10, wherein step a) comprises contacting the fabric with the fluid dry cleaning composition at a pressure between 2 and 25 MPa.

23. 01. 2002

ABSTRACT

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The present invention provides a method for the removal of stains from fabric using densified carbon dioxide. More particularly the invention is concerned with a method of dry
5 cleaning fabric comprising the successive steps of (a) contacting the fabric with a fluid dry cleaning composition containing densified carbon dioxide at a temperature between -20 and 60°C and a pressure between 1 and 100 MPa., so as to allow stains to dissolve and/or to disperse into the fluid dry cleaning composition and (b) separating the fabric and the fluid dry cleaning composition; wherein the fluid dry cleaning composition comprises an ionic
10 surfactant in a concentration of between 0.01 and 15% by weight of the carbon dioxide and wherein during step a) at least 10%, preferably at least 30% of said ionic surfactant is present in undissolved form.

It was surprisingly discovered that the use of an ionic surfactant, e.g. a surfactant that
contains a lipophilic alkyl residue and a polar amine or carboxylate residue, produces
15 exceptionally good cleaning results if said surfactant is employed in an amount that exceeds its maximum solubility in the densified carbon dioxide composition.